THE DIAGENESIS AND PETROLOGY OF IRON OXIDES IN THE GARBER-WELLINGTON FORMATION

BY

JESSICA EILEEN WITT

Bachelor of Science

Northwest Missouri State University

Maryville, Missouri

1999

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
May, 2001

THE DIAGENESIS AND PETROLOGY OF IRON OXIDES IN THE GARBER-WELLINGTON FORMATION

Thesis Approved:

Zuhair al-Shaieb
Thesis Advisor

Stanley T. Paxton

Jon Puckette

Dean of the Graduate College

ACKNOWLEDGEMENTS

This study attempts to delineate the diagenesis of iron oxides using petrographical analysis. The interactions of iron oxides between quartz and carbonates within the Garber Sandstone were studied in detail. In order to accomplish this objective, the geochemistry and petrography of outcrops in the Central Oklahoma Aquifer from the Garber Sandstone were examined in Oklahoma County. The relationship of red-beds in a continental setting is also discussed along with the type of carbonate cements and their environmental implications for the diagenesis of the Garber Sandstone.

The writer wishes to express her appreciation to Dr. Zuhair Al-Shaieb, thesis adviser, for his guidance, assistance, and many insightful discussions throughout the study and time spent at Oklahoma State University. Dr. Jim Puckette and Dr. Stan Paxton, thesis committee members, for their discussion of theoretical ideas of diagenetic processes and for their critique of the manuscript. Special thanks are also due to Brad Brittain and Tom Kropatsch for fieldwork during the course of the study.

Lastly, the writer would like to thank her family for their emotional support. The most important thought in geology is that it is a visual science. We can readily observe rocks and Earth's processes as long as one is open to ideas.

TABLE OF CONTENTS

LIST OF FIGURES

Figure Page

CHAPTER ONE

INTRODUCTION

The Central Oklahoma Aquifer also known as the Garber-Wellington Aquifer, consist of Permian age siliciclastic rocks that contain quartz, porosity and cements (hematite and carbonates). The importance of the investigation lies in the rock interface (i.e.: the relationship of the grains, cements and matrix). The present investigation is part of a regional analysis of the Permian Garber and Hennessey being conducted by the Oklahoma State University School of Geology. The focus of this thesis investigation is on the petrology of the Garber Sandstone with emphasis on the iron oxide cements.

Objectives

The objectives of this study are to: (1) to document the relationships of the framework of grains to the cements, (2) determine porosity type(s), (3) establish the diagenetic sequence for the Garber Sandstone in the Central Oklahoma Aquifer and (4) determine the geochemistry of iron oxide cements that fill the pore spaces in the Garber Sandstone.

Area of Investigation

The Central Oklahoma Aquifer underlies about 3,000 square miles (7770 km^2) (Figure 1) of central Oklahoma (parts of Cleveland, Logan, Lincoln, Oklahoma, Payne, and Pottawatomie Counties) according to Parkhurst, Christenson and Breit (1993).

The locality of the investigation within the Central Oklahoma Aquifer that was studied was in and around the City of Edmond, in Oklahoma County. The present investigation is restricted to the outcrops from the Garber Formation, which crop out in Oklahoma County, Oklahoma. Oklahoma County is bounded by Logan County on the north, Lincoln and Pottawatomie Counties on the east, Cleveland County on the south and lastly, Canadian County on its western boundary. The outcrop localities are bound by the coordinates of 97°30'00''W and 36°40'00''N. Major geographic features of the study area within the aquifer are the Deep Fork River, North Canadian River and Lake Hefner. Besides Edmond, other important cities include Midwest City, Oklahoma City and Del City (Figure 2).

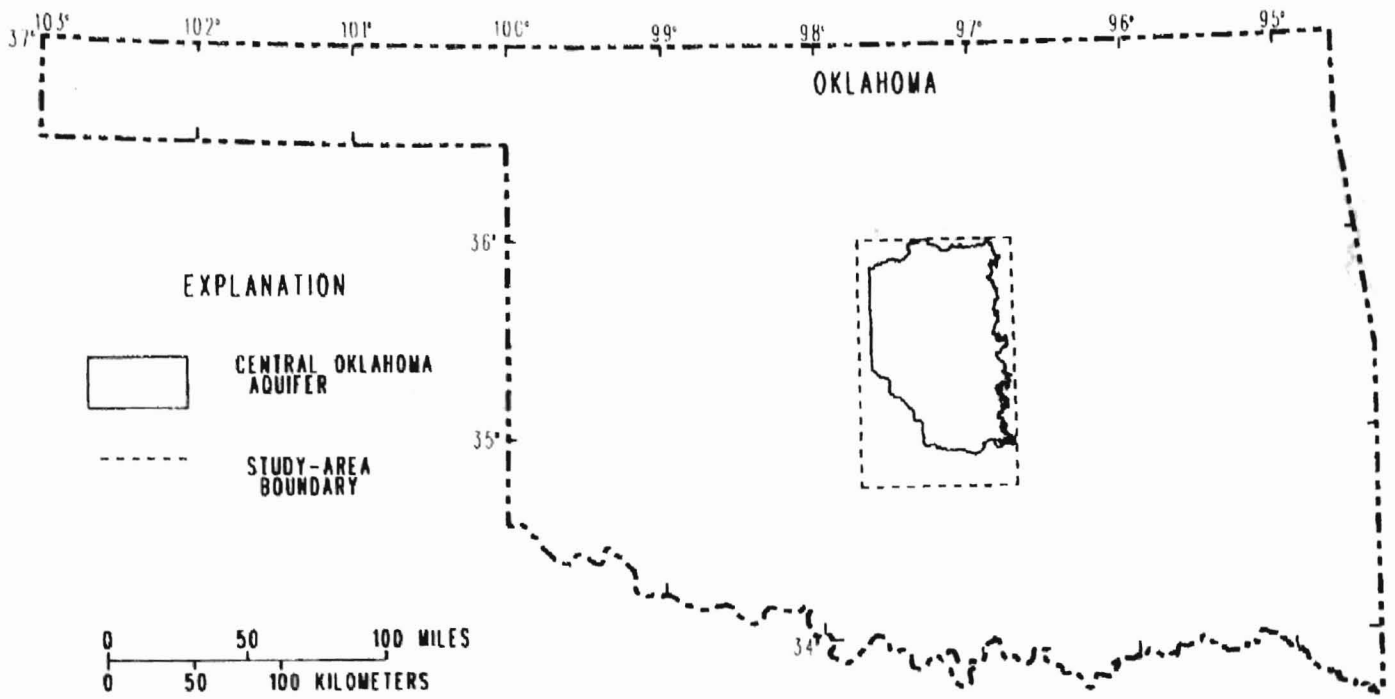


Figure 1. Location of Central Oklahoma Aquifer and Study Area (Parkhurst, Christenson and Breit, 1993)

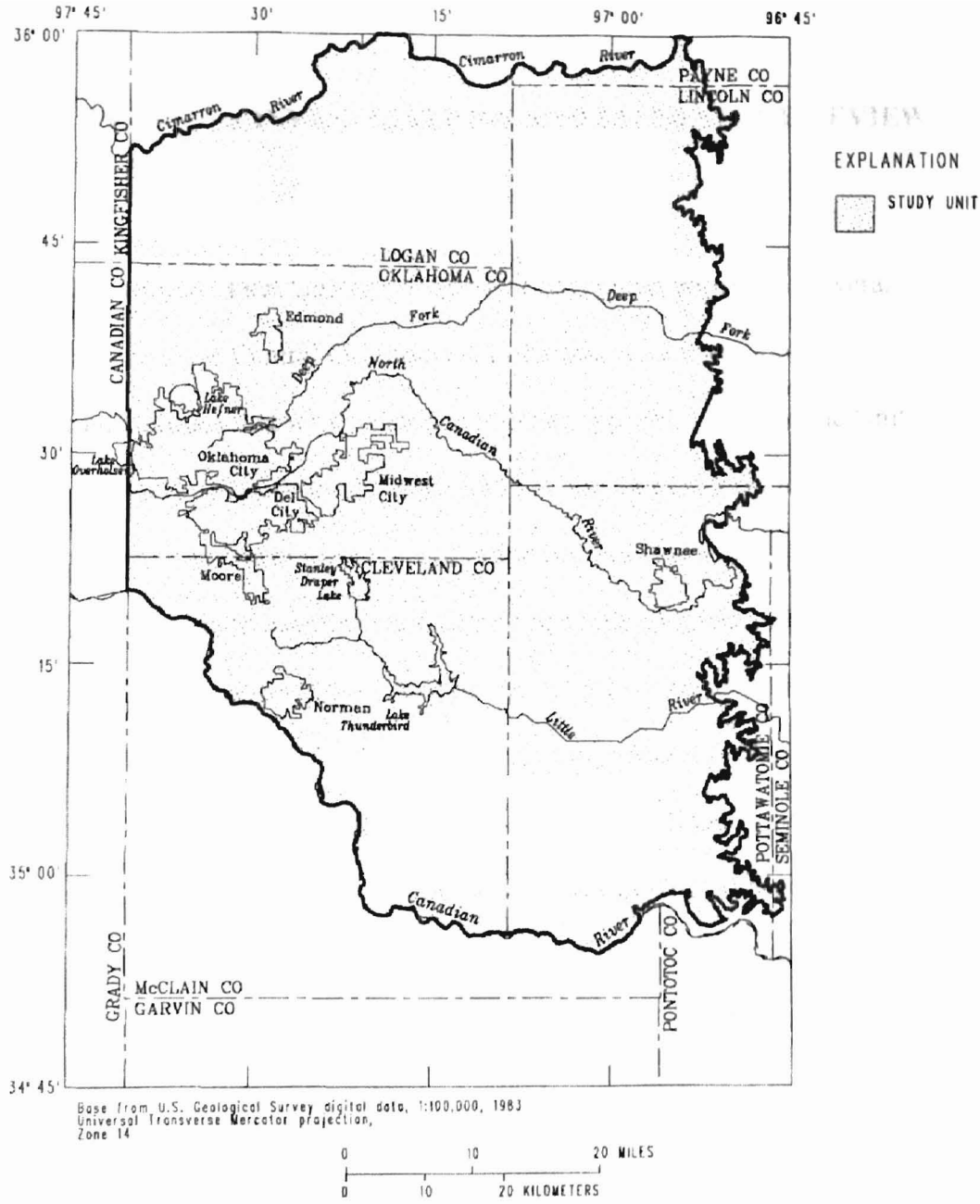


Figure 2. Major Geographic Features of the Study Area (Parkhurst, Christenson and Breit, 1993)

CHAPTER TWO

PREVIOUS INVESTIGATIONS AND LITERATURE REVIEW

The United States Geological Survey (USGS) has performed several investigations of the Central Oklahoma Aquifer that have been done prior to this study. The documentations that were examined in relation to this study are the United States Geological Survey Water-Supply Paper 2357-A and Open File-Report 92-642. These reports were to implement, develop and refine the National Water-Quality Assessment (NAWQA) Program to examine the Central Oklahoma Aquifer. The United States Geological Survey papers that summarize the different aspects of the Central Oklahoma Aquifer are the following: (1) Summary of Investigations, (2) The Diagenetic History of Permian Rocks in the Central Oklahoma Aquifer, (3) Geochemical Characterization of Solid-Phase Materials in the Central Oklahoma Aquifer, (4) Summary of Geochemical and Geohydrologic Investigations of the Central Oklahoma Aquifer and, (5) Arsenic, Chromium, Selenium and Uranium in the Central Oklahoma Aquifer.

Purpose

This research is to determine the relationship between the quartz grains and the pore filling cements: calcite, dolomite and Mn-rich hematite. The Garber Sandstone is

of lower Permian in age (Leonardian). It is characterized by lenticular bed of fine-grained, cross-bedded sandstone that is interbbeded with siltstone and mudstone (Parkhurst, Christenson and Breit, 1993). The Garber coloration at the surface is due to iron oxides; the color ranges from a pale red to reddish-brown. The Garber at the surface is subdivided into the Lucien Shale Member and the Hayward Sandstone Member (Cox, 1978). Red beds are usually continental deposits belonging to the Late Paleozoic, early Mesozoic and Late Cenozoic Eras They occur in the Permian, Triassic and Jurassic Periods. It has been suggested that the detrital hematite originates from weathering of eroded red soils. These form of detrital hematite forms in a semi-arid climate with wet-dry cycles and a low-carbon environment. Due to terrestrial weathering of red beds, the major components to be considered in silicate weathering are Na_2O, K_2O, MgO, CaO, FeO, Fe_2O_3, Al_2O_3, SiO_2 and CO_2. These components exist in the aqueous phase: K^+, Na^+, Mg^{2+}, Ca^{2+}, Fe^{2+}, H_4SiO_4, HCO_3^-, H_2CO_3 and monomeric hydrophilic polymers and organic complexes of Al^{3+} and Fe^{3+} (Yariz and Cross, 1979). This weathering favors the formation of hematite through ferrihydrite. This formation of hematite requires the re-mobilization of iron during diagenesis (Cornell and Schuertmann, 1996).

The chemical weathering of iron minerals is complex because most iron mineral-soil water interactions involve oxidation-reduction reactions and may also involve the formation of several residual solid phases. Most iron minerals such as magnetite, siderite, pyrite, pyrrhotite, and iron silicates usually occur dispersed throughout the rock, in bands or segregations. During the weathering process, ferrous iron is oxidized by O_2 in the soil-water interface to ferric ion, which hydrolyzes to form ferric oxides.

These minerals (goethite, lepidocrocite, hematite and maghemite) form as alteration products that are yellow, orange-brown and red in color. The weathering usually results in colored soil zones that have a sharp contrast compared to the surrounding outcrops (Garrels and Mackenzie, 1971).

In the weathering zone, iron to form oxide minerals is due to low solubility under oxygenated conditions. Hematite is the stable species when compared to goethite, lepidocrocite and maghemite. Hematite has the tendency to develop in the soils of warm, well-watered regions (Garrels and Mackenzie, 1971).

Red beds, and more specifically, Mn-iron oxides (hematite) form in oxidizing environments. Mn-hematite can form by the leaching of Mn and Fe by aqueous solutions of various organic acids. This showed that Mn is more concentrated than Fe in solutions from weathered rocks, where Fe is oxidized (Yariz and Cross, 1979). The oxidation rates of Fe (II) and Mn (II) and or precipitation of hydrous oxide of the metal greatly increased with an increase in pH. The oxidation is catalyzed by the presence of colloid materials that are in suspension. Another catalyst for the oxidation of Fe and Mn are clay minerals. Hence, the rate of oxidation increases with higher surface area of the clay minerals.

There are two main hypothesizes for the formation of hematite coatings. The first hypothesis requires groundwater containing soluble Fe and Mn (reduced) that enters oxygenated water flowing in streams (Carpenter, 1975). The second hypothesis of hematite coatings is possibility due to an increase in the age of the sands allows for greater time for weathering processes to develop the hematite coatings around quartz grains (Dorn, 1998). Iron oxides have a strong adherence to quartz surfaces because of

the formation of chemical Fe-O-Si bonds (Scheidegger et al, 1993). If the rock is stable, the more likelihood it will be coated.

CHAPTER THREE

GEOLOGICAL SETTING

Sir Roderick Impy Murchison named the Permian Period in 1841 after the Russian province of Perm. In the United States, Major Frederick Hawn (Kansas), and Benjamin Franklin Shumard (Texas) first documented Permian rocks in 1858 (Petersen, Rigby and Hintze, 1980). The Permian Period spans approximately 290 to 240 Ma. It is bounded below by the Pennsylvanian age rocks and above by sediments of the Triassic Period.

Within the United States, Permian strata occur almost entirely in the western half. The strata occur in the states of Arizona, New Mexico, Texas, Oklahoma, Kansas, Colorado, Utah, Nevada, California, Idaho, Montana and Wyoming and Alaska. In the western United States, Permian strata are extensive in the subsurface because they are concealed under Mesozoic and Cenozoic rocks. Permian strata previously extended over the Great Basin region but are not present today because erosion has cut down to Pennsylvanian and Mississippian rocks at the surface (Miller, 1942). There is a portion of the Permian section preserved in the Appalachians.

During the Early Permian, an interior sea was spread over Nebraska, Kansas, western Oklahoma, central and western Texas, New Mexico and eastern Colorado and

Arizona. This sea was also connected to the Gulf of Mexico through eastern Mexico. Also during the Early Permian, California and Alaska were submerged by the Pacific Ocean. Early Permian strata in the Appalachian region are characterized by fresh-water swamps/basins and high plant growth (Miller, 1942). In the south, continental glaciations moved down from the South Pole. At the same time, evaporites and eolian sandstones were being deposited in the Northern Hemisphere in the areas of Europe, North America and China. Red beds and evaporites are today distributed in the former Gondwanaland, areas of South America and northern Africa (Scholle, Peryt and Ullmer-Scholle, 1995).

Middle Permian time had the interior sea enlarging and connecting with the Pacific Ocean. During this time, the interior sea submerged Northern California through Alaska. The Ancestral Rocky Mountains were slowing rising during this time. These mountains cutoff the sea on the east. During or after the cutoff of the sea, coral reefs began to form and acted as a barrier separating the basin from the sea on the west. This interval of the Middle Permian is when arid conditions were most favorable for the formation of red beds (Miller, 1942).

In Late Permian, red beds and evaporates were widespread in central Pangea. There were increases in aridity (Scholle, Peryt and Ullmer-Scholle, 1995). By this point, the western seaway was almost obliterated, leaving only western Texas, southern New Mexico, and eastern Mexico submerged. At the end of the Permian, the sea was completely gone from North America (Miller, 1942).

The climate of the Permian Period ranged from extensive glaciation over low-latitude areas in the Southern Hemisphere of Pangea to areas of widespread aridity in

the Northern Hemisphere in areas of North America and Europe, before the last breakup of Pangea (Petersen, Rigby and Hintze, 1980). The general retreat of the seas from the continents resulted in reduced subsidence reducing temperatures and heavy precipitation on the windward side of the new mountain ranges and low precipitation on the eastern side. These characteristics all in part are due to tectonics of mountain building that resulted in small and large uplifts of the continent (Miller, 1942).

Stratigraphy

The Stratigraphy of the Garber-Wellington portion of the Central Oklahoma Aquifer, consist mainly of the Garber Sandstone and the Wellington Formation of the Sumner Group (Permian age) (Figure 3). The chronological orders of the formations within the aquifer from youngest to oldest are the following:

1- Hennessey Group

2- Garber Sandstone/Wellington Formation

3- Chase, Council Grove and Admire Groups

4- Vanoss Formation

The Permian geologic units are the Hennessey through the Admire Groups. The Pennsylvanian geologic unit and the oldest unit within the aquifer is the Vanoss Formation. Above the Permian age strata are Quaternary terrace and alluvial deposits that fills the incision of the Deep Fork and North Canadian Rivers.

The Hennessey Formation is composed of reddish-brown shale, mudstones and siltstone with a few beds of very fine-grained sandstone. Underlying the Hennessey is the main portion of the Central Oklahoma Aquifer: the Garber/Wellington Formation. The Garber Sandstone and Wellington Formation have similar lithologic characteristics. The Garber is described in the upper part as being a fine-grained, light pink to red sandstone; where-as the lower part is a darker red to brown sandstone of similar grain size to the upper portion of the Garber Sandstone.

Characteristics of the outcrop localities seen in the study area include: (1) the upper part contains nodules, (2) dark interbedded red to purple molted sandstone, (3) the beds can be massive to thin bedded, (4) sandstone can be lenticular shaped lenses, (5) limonite enrich, (6) upper part of the Garber is well cemented and the lower Garber is poorly cemented, (7) pebble conglomerate and (8) white-gray dolomite. The Wellington Formation within the aquifer consists of more of a mixture of sandstone, siltstone and mudstones. Because of similarities in lithology the United States Geological Survey has classified the Garber Sandstone and Wellington Formation as one unit (Parkhurst, Christenson, Breit, 1993).

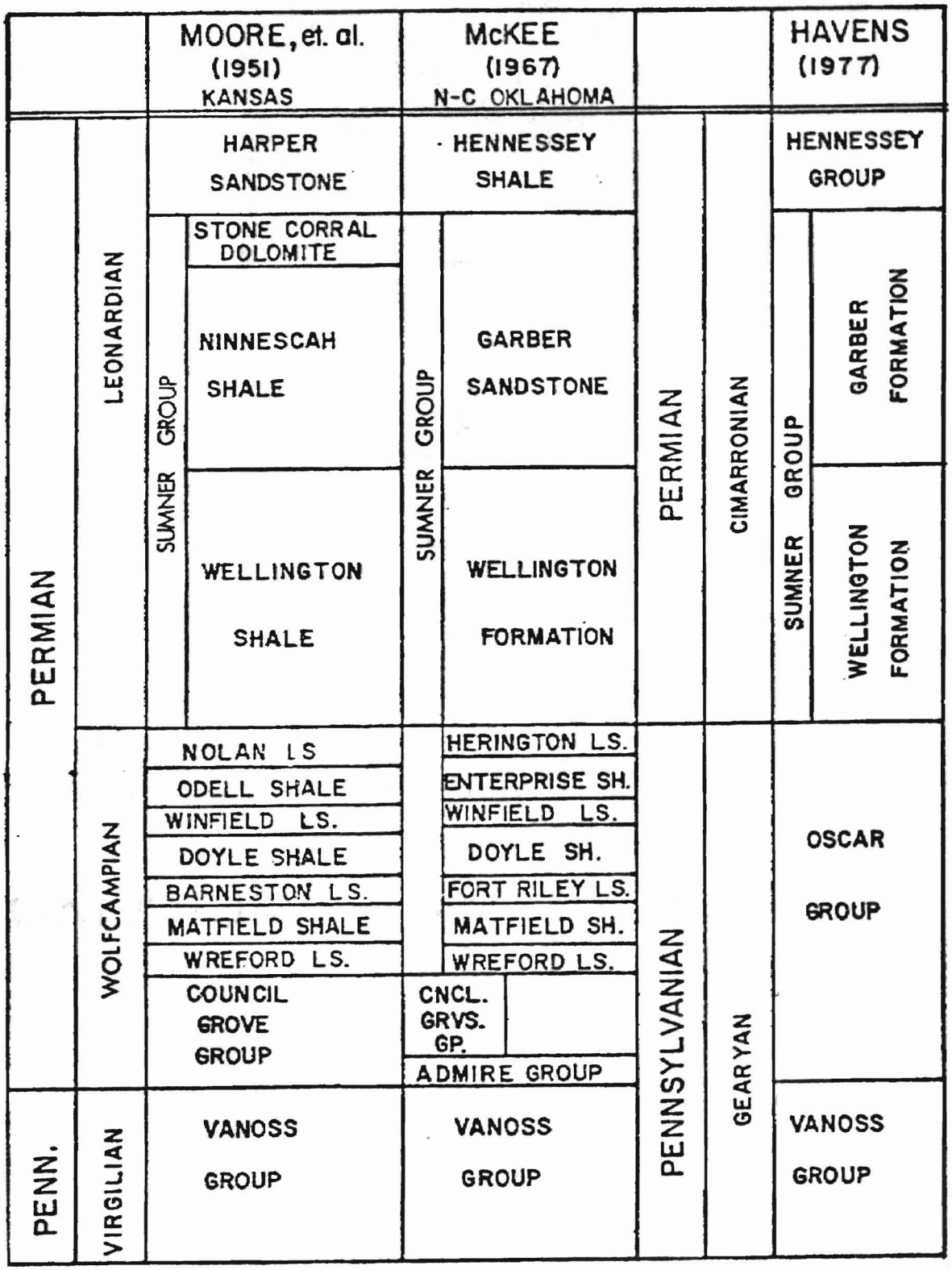


Figure 3. Stratigraphic Chart of Permian and Pennsylvanian Units (Elrod, 1980)

Figure 4 (a). Cross Bedding Feature found on Coffee Creek Road, Edmond.

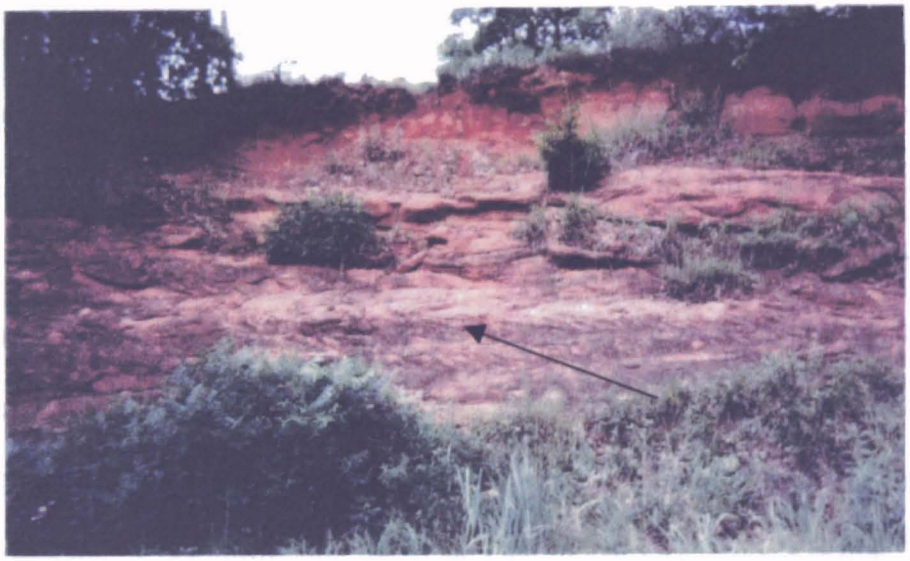


Figure 4 (b). Trough Cross Bedding Feature found Douglas Road, Edmond.

Sedimentary structures that were observed in outcrops include trough cross bedding, root traces, upward dips of beds, herring bone structure and friable ledges of calcrete nodules (Figure 4a and 4b). Underlying the Garber/Wellington Formation are the Chase, Council Grove and Admire Groups. They are composed of lithologies of fine-grained cross-bedded sandstone, shale and thin limestone. The oldest formation, the Vanoss, consist of shale and mudstones and thin, fine-grained sandstone (Parkhurst, Christenson, Breit, 1993).

CHAPTER FOUR

METHODOLOGY OF INVESTIGATION

The sample methodology for this study was to collect field specimens at different outcrops based on their variations in cementation, color, structure and texture. Approximately thirty field samples were collected for thin section petrographic analysis.

The thin sections were examined using a polarizing microscope. The microscope was used to identify the quantity of the grains, cements and porosity and types of grains, cements and porosity seen within the individual thin sections. Determination of the point counts ten times in different location on each slide was through the one-millimeter bar-scale seen in the microscope's ocular.

The study was designed to have a better understanding of the outcrop constituents in relation to the groundwater constituents. This study will be further used by the Oklahoma State University effort to help understand the formations within the

Central Oklahoma Aquifer, focusing on the Garber-Wellington and Hennessey Formations.

CHAPTER FIVE

PETROLOGY, PETROGRAPHY AND DIAGENESIS

Detrital Constituents

The major framework grains of Permian rocks in the study area are monocrystalline quartz with minor amounts of plagioclase, rock fragments (carbonate, siltstone, chert, polycrystalline quartz and metamorphic). Trace detrital constituents are muscovite, zircon and tourmaline.

The relative abundance of the framework minerals varies among outcrop locations. This variation is due to weathering. Sandstone in the study unit is classified mainly as a quartz arenite (Figure 5) (Folk, 1980). The sandstone is fine-grained and moderately sorted; constituent grains are subrounded to subangular according to Scholle (1979).

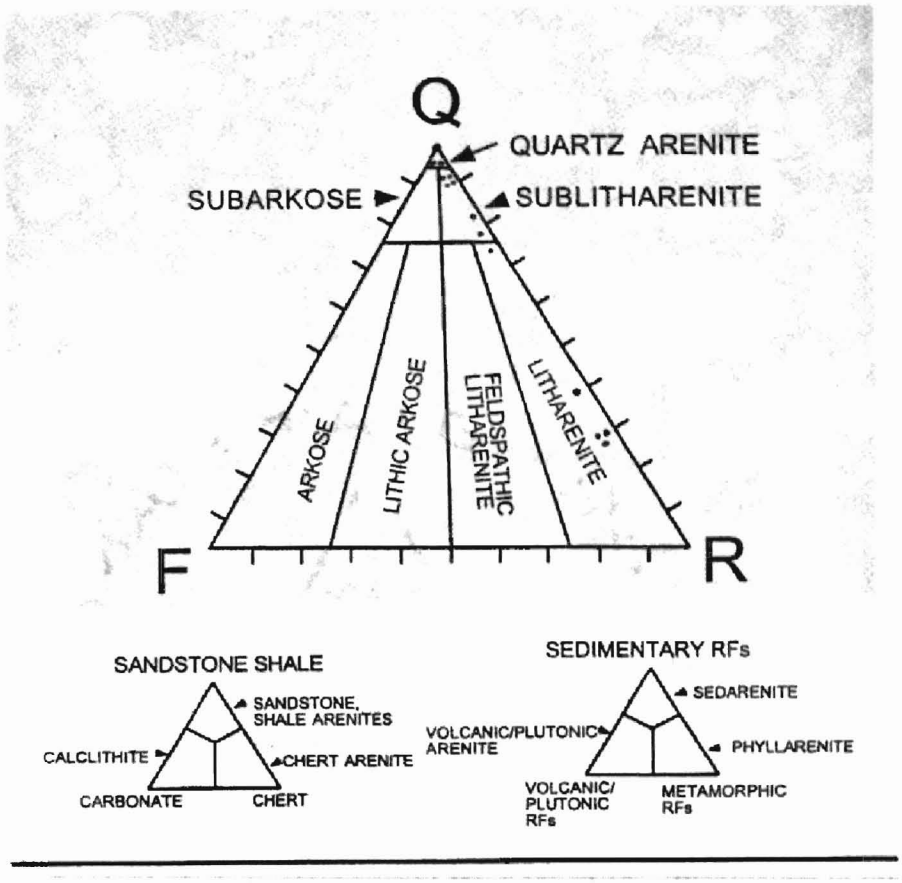


Figure 5. Folk Diagram (Folk, 1980). Garber Sandstone is a Quartz Arenite

The percentage of monocrystalline quartz as is seen in thin sections ranges from 72% to 9%. The monocrystalline quartz has characteristics of undulose extinction, vacuole inclusions and embayments (Figure 6). The polycrystalline quartz has a range from 5% to 2% with extinction patterns possibly suggesting metamorphic origin (Folk, 1980).

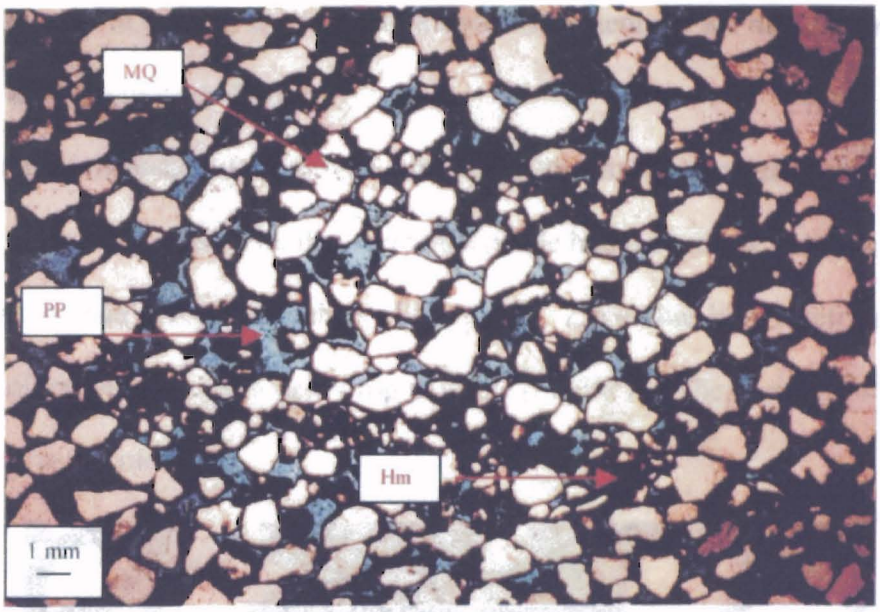


Figure 6. Monocrystalline Quartz (MQ), Hematite Cement (Hm) and Primary Porosity (PP) in Plane Polarized Light 100X

The percentage of plagioclase ranged from 4% to 1%. Plagioclase in thin section was either (1) albite twinned or contained (2) clear interiors with good cleavage. Most of the feldspars have been corroded; partially dissolved, leaving voids and broken fragments. The feldspars are best preserved in samples that contained illite matrix or dolomite cement.

The observed rock fragments were chert, carbonate and metamorphic varieties. The chert ranged from 4% to 1%. The chert grains are commonly corroded, oval to circular in roundness and coated by hematite cement or illite clay The carbonate rock fragments observed in conglomerates in dolomite. No calcite was present. The percentage values ranged from 45% to 4%. The carbonate rock fragments are commonly enclosed by illitic clay and hematite cement. The metamorphic rock fragments observed

in minute amount in volume as in schist. Major components of the metamorphic rock fragments are muscovite and quartz.

Trace constituents of muscovite, zircon and tourmaline were also seen in thin section samples. The muscovite that were observable had percentage values of 3% to 1%. The zircon had percentage values of 5% to 1%. Zircon has high birefringence, is purple in coloration and oval to tear drop in shape (Figure 7). The tourmaline had a value of 2% and orange coloration.

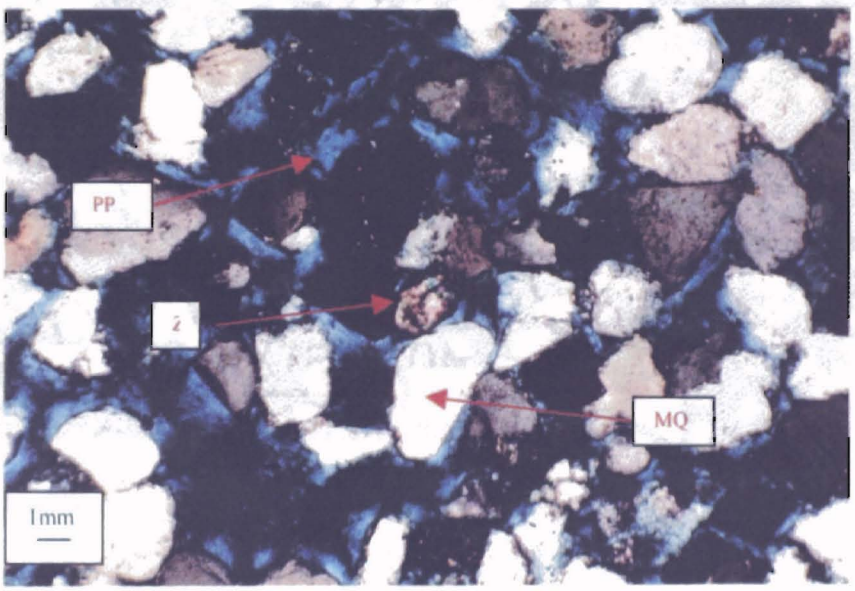


Figure 7. Zircon (Z), Monocrystalline Quartz (MQ) and Primary Porosity (PP) 100X

The clay minerals that were observable in the Garber Sandstone were illite, chlorite and muscovite. Illite is seen with hematite cement. The chlorite grains were seen as an oval to round pale green grain. It is suggested that further analysis of clay minerals in the Garber Sandstone with X-Ray Diffraction (XRD) analysis be analyzed in further detail.

Authigenic Constituents

Dolomite, calcite and hematite all formed after the deposition of detrital sediments. These minerals were seen as matrix, pore-filling cements and as coatings on detrital grains (Figure 8).

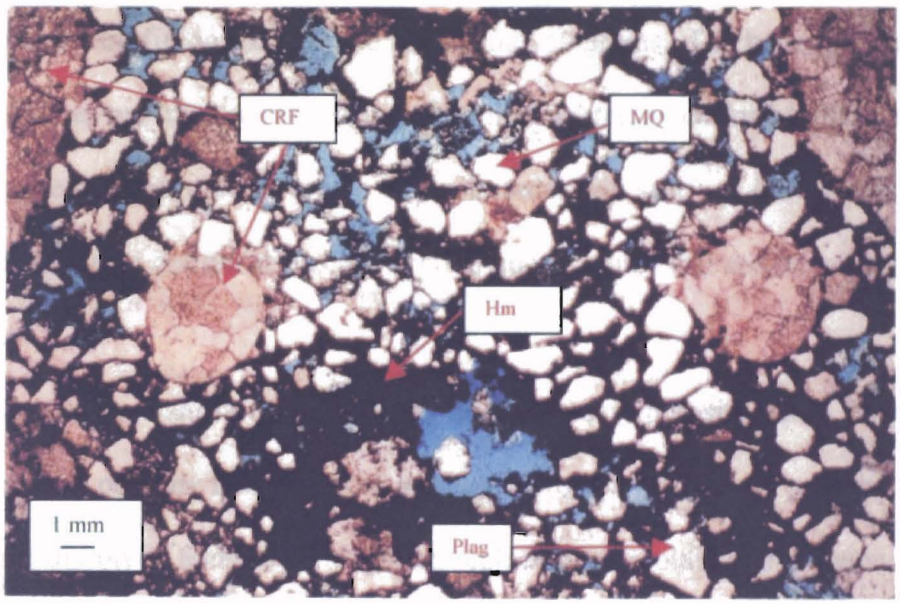


Figure 8. Hematite cement (Hm) coating detrital grains of monocrystalline quartz (MQ), plagioclase (Plag) and carbonate rock fragments (CRF) 100X

Sparry dolomite is one of the most abundant authigenic minerals in the study area. It is found as rhombs, pore-filling (bridging) cement, patches/clusters and as replacement of dolomite nodules found in conglomerate samples. Evidence of dissolution of sparry dolomite is irregular, intermittent, spherical patchworks of continuous pore-filling dolomite cement. The rhombs of dolomite within the matrix (displacement) is suggestive of the dolomite forming prior to the matrix.

Calcite is minor cement in the Garber Sandstone occurring as nodules. Within the sandstone it occurred as circular, sparry patches that are continuous. The calcite patches of cement usually have 20 to 40 neighboring grains in its patch framework in the nodule.

The dominant mineral seen within the area of investigation is hematite. The occurrence of hematite is in the form of Liesegang bands within the sandstone, disseminated pore-filling patches and as coatings on grains. The hematite when seen in thin section has red internal reflections when illuminated by oblique light. Hematite is found as fine grained, reddish brown to black under thin section. It occurred in the void spaces, coatings on detrital grains and around quartz grains that are cemented by dolomite or calcite.

The Garber Sandstone has primary and secondary porosity types. The dominant type is primary porosity that occurs as granular porosity. Secondary porosity occurs in the form of dissolved feldspars and quartz, replacement, moldic and as veins. Primary porosity has a range from 27% to 1%. Secondary porosity has a range of values from 37% to <1%. The total amounts of primary and secondary porosity for the Garber Sandstone that range from 37% to <1%.

Diagenesis

The diagenesis of the study area can help to explain some geologic processes that have influenced the appearance of the present outcrops. The processes that have influence the Garber Sandstone are deposition, burial and exposure began during the Permian time to the present. The detrital grains were subaerial dissolved and or altered

and authigenic cements and grains were dissolved and precipitated due to the change of fluid compositions in the pore space. The changes in detrital and authigenic grain composition were due to climatic changes and sea-level fluctuations. The climatic changes included transition from wet to dry periods and sea level fluctuations that occurred during deposition and during burial (movement of sea water and flow of meteoric waters).

Deposition

The area of investigation is in a continental setting. During Permian time, the area had mainly fresh-water with recharge coming from the southeast. As sea level rose, marine water inundated the study area. Evidence: Dolomite rhombs within clay matrix; monocrystalline quartz.

The Permian had dry climate. Soil-forming by-products such as carbonate nodules and purple molted sandstones seen on outcrops are suggestive of a dry Permian climate. Evidence: Carbonate Rock Fragments; hematite.

During the wet periods of the Permian, clays and hematite formed due to chemical weathering of pre-existing rocks in the area. As the fresh water increased in its discharge, silicon and iron were redistributed. The reddening of hematite occurred diagenetically during deposition and burial. Evidence: Hematite cements in the conglomerate thin section samples.

After the wet cycle, an even drier climate prevailed. Evidence: Dissolution of feldspar grains within the dolomite cement.

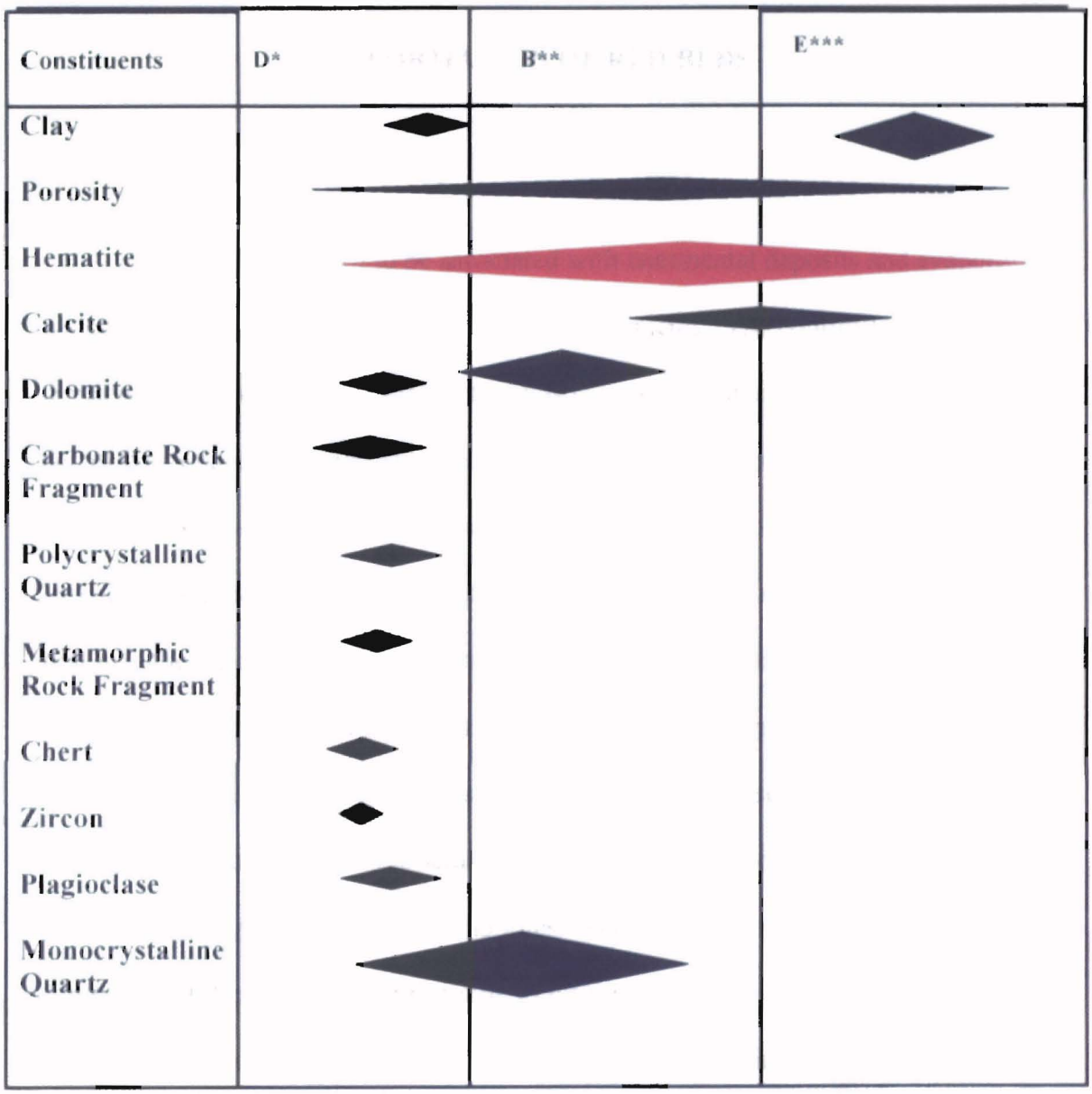
Burial

Burial of the study area occurred only a few feet till erosion. Saline waters formed by evaporation were the main fluid in the pore space. Evidence: Dolomite cement and some hematite; preservation of primary porosity.

Exposure

Meteoric water from direct precipitation served as the recharge for the aquifer. Evidence: Calcite cement (Christenson and Havens, 1998).

Chart I: Diagenetic Sequence of Events: Deposition, Burial and Exposure from Permian to Quaternary



* Deposition (D)
** Burial (B)
*** Exposure (E)

CHAPTER SIX

FORMATION OF RED BEDS

Red beds are known to be associated with continental deposits and evaporites, which are indicative of desert or subdesert environments. The controversy on the development of red hematite pigment in clastic rock sequences has a long history. The debate has focused on whether or not physical and chemical parameters of moist versus arid climates have played a role in the formation of red beds. The two main hypothesizes concerning the origin of red beds were that of Krynine and Walker. The first hypothesis, by Krynine, contends that erosion and deposition of hematite stained the soils. Hence, the hematite is detrital and the sediments are red at the time of deposition when deposited. The hematite formed in lateritic soils in wet tropical or subtropical source areas. These sediments are transported and deposited in desert basins, becoming associated with evaporites. The second hypothesis, by Walker, contends that the deposition of hematite to form red beds is by hot and arid climates. The hematite formed in situ by alteration of iron bearing detrital grains. Therefore, the hematite is authigenic, and the sediment was not red when original deposition occurred (Walker, 1967a). This mechanism requires the (re-) mobilization of iron during diagenesis.

The most pressing question for the Garber Sandstone in relation to the genesis of red beds is: What type of climate enhances the development of red hematite pigment

and the consequent genesis of red beds? The formation of hematite in the presence of water according to the Gibbs Free Energy (-492.1 +/ 1.5 kJ mol ¯1) suggests that red beds can form in either humid tropical or hot arid climates. Based on field and petrographic data, the Garber Sandstone was formed in a hot, dry climate. The field data has been representative of alluvium sediments. The petrographic evidence indicates that hematite pigment formed in place after the sediments were deposited as is noted b t he hematite cement in contact with individual grains found in thin section (Walker, 1967a). The hematite pigment has formed diagenetically in sediments that were deposited in arid climates. The hematite pigment reflects interstitial chemical conditions that support in situ formation and preservation of hematite within the depositional basin (Walker, 1967b).

Red beds are characterized by their distinctive red color caused by iron oxides in a continental setting. Hematite under petrographic microscope occurs in many forms. The six forms of hematite in sedimentary rocks according to Cornell and Schwertmann (1996) are the following: (1) ultrafine red pigment, (2) coarse (2-40um) specular hematite, (3) large size of grains and euhedral shape, (4) starlike twins, (5) primary (detrital hematite as coatings and as impregnations of rock fragments), and (6) authigenic and idiomorphic hematite crystals several mm in size and arranged in aggregates.

Geochemistry

The geochemistry of red beds is primarily related to the formation of hematite through weathering and erosion of iron bearing minerals such as pyroxenes, amphiboles, iron rich phyllosilicates (biotite), and lithic rock fragments from metamorphic and igneous sources. Erosion and weathering aid in the development of ferric ions to form free iron, which is essential in the formation of hematite. The ferric ions are derived from the release and oxidation of ferrous ions. Free iron can also be formed in clay minerals. The free ion can serve as a good catalyst for the oxidation of Fe and Mn as well. The oxidation is catalyzed by the presence of Fe colloid materials in suspension (Yariv and Cross, 1979).

Free iron in the ferric state has a valence of 3^+ and ferrous ion of 2^+. The higher the pH of the solution, the more rapidly the Fe^{2+} ions will dissolve and become oxidized (Cornell and Schwertmann, 1996). The stability relationship for the system Fe-O-H_2O-Fe_2O_3 at 25 degrees Celsius at 1 atmosphere, assuming ΣS=10^-6 (Figure 9) (Krauskopf and Bird, 1995). The approximate pH for hematite in solution is 7 with the redox potential (Eh) around 0.30 to 0.40.

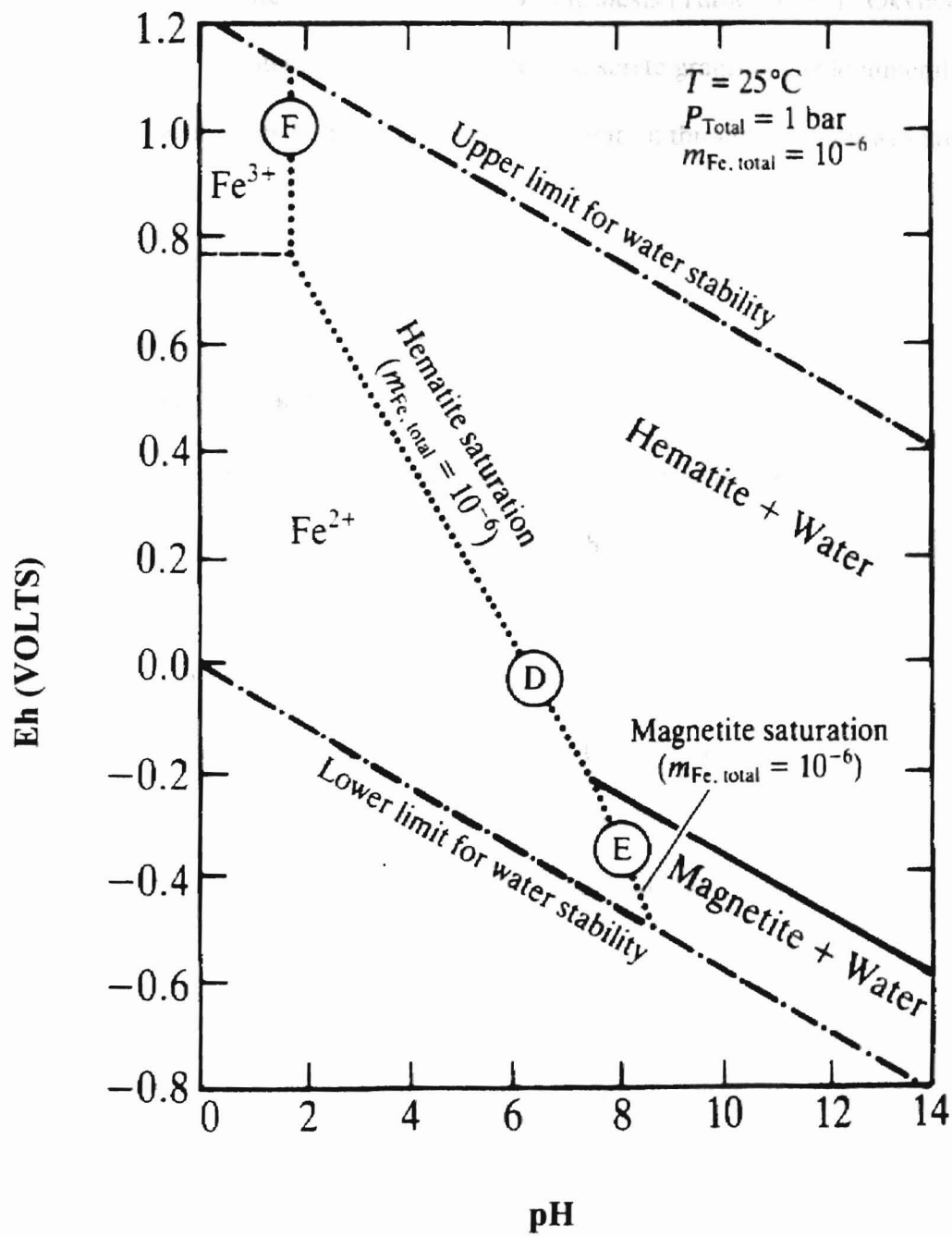


Figure 9. Eh-pH Diagram of Hematite and Water (Krauskopf and Bird, 1995).

In conditions where soil and sediments are not in strongly reducing environments, oxyhydroxides exist. An example of ferric oxyhydroxides is limonite, which is derived from goethite. Limonite in this study has been formed through the

precipitation from interstitial waters during diagenesis (Turner, 1980). Oxyhydroxides occur as coatings around silicate grains and as discrete grains of oxide mineral (Drever, 1997). Limonite alters to hematite during dehydration through the following reactions (Schmalz, 1968):

$$2Fe(OH)_3 \longrightarrow Fe_2O_3 + 2H_20 \qquad (6.1)$$

$$2Fe(OH)_3 \longrightarrow 2HFeO_2 \longrightarrow Fe_2O_3 + 3H_2O \qquad (6.2)$$

$$2HFeO_2 \longrightarrow Fe_2O_3 + H_2O \qquad (6.3)$$

The transformation of goethite into hematite is based on the parameters of pH, temperature and water activity. The pH affects the rate of dissolution and solubility of speciation of iron in solution. Increasing the temperature of limonite induces dehydration and promotes hematite while decreasing goethite. The higher the temperature, the higher the pH needs to be in order to form hematite in the product of the reaction. The water activity or the relative humidity for goethite/hematite equilibrium is related to aqueous systems (Cornell and Schwertmann, 1996):

$$2FeOOH \longrightarrow Fe_2O_3 + H_2O \qquad (6.4)$$

It is very rare for hematite to be the only iron oxide in a system but it is associated to an extent with goethite. Goethite is an ubiquitous iron oxide found in small concentrations in consolidated and unconsolidated rocks of any age. The dark red color of hematite usually masks the yellow to brown goethite. The formation of hematite and goethite in relation to toposequences is that the red soil occurs on the dry slopes and grade into yellow soils in the wet depressions. In the yellow zones there are more reduction taking place than oxidation. In warmer environments, goethite is often

associated with hematite. It is found on outcrops as mottles and as concretions (Cornell and Schwertmann, 1996).

In a natural calcareous environment with oxidized Fe^{2+} and the presence of $CaCO_3$ (calcite), calcite neutralizes the protons transpiring from hydrolysis of Fe^{3+}:

$$4Fe^{2+} + O_2 + 4CaCO_3 + 2H_2O \longrightarrow 4FeOOH + 4Ca^{2+} + 4CO_2 \qquad (6.5)$$

Goethite will only form if CO_2 is present. Due to the low solubility of $CaCO_3$, the formation of goethite would not proceed (Cornell and Schwertmann, 1996).

Iron Oxides Occurrences

Hematite cement is responsible for the red coloration of the Garber-Wellington Formation. In the study area, hematite occurs in the Garber as ultrafine red pigment and authigenic crystals several millimeters in size and arranged in aggregates. The ultrafine hematite occurs as coatings on detrital grains. The hematite within the sandstone forms coatings and cement in the pore space. Hematite also occurs mixed with carbonate cements as patches, bands and coatings (Figures 10 and 11).

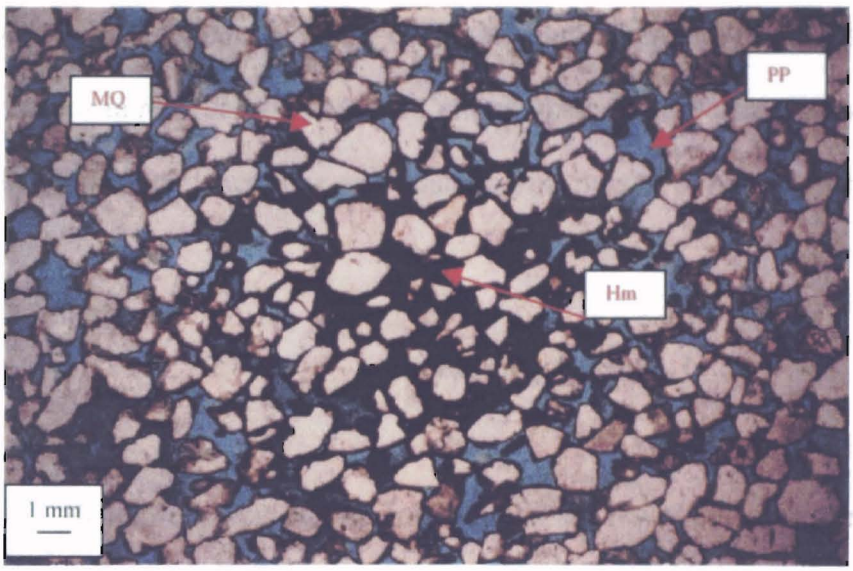


Figure 10. Monocrystalline quartz (MQ), primary porosity (PP) and hematite (Hm) patchwork in plane polarized light 100X

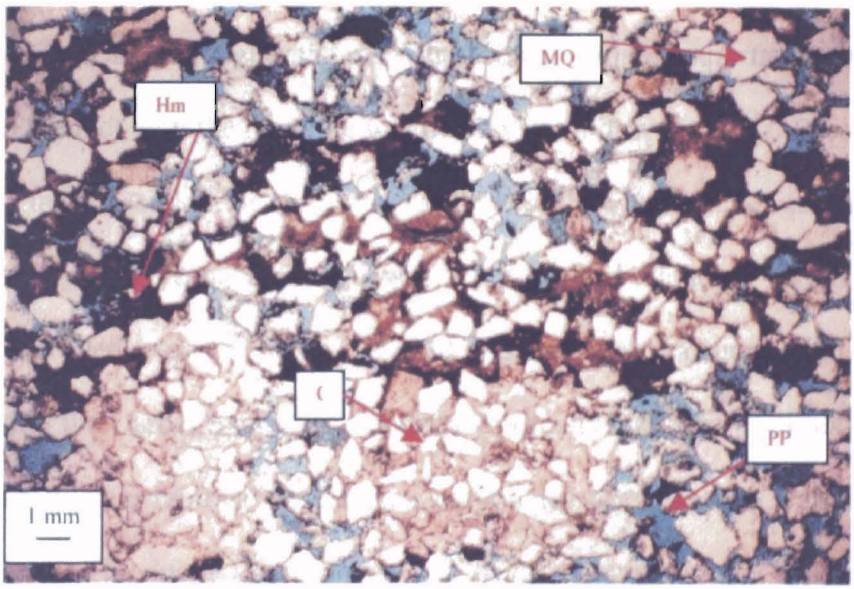


Figure 11. Monocrystalline quartz (MQ), primary porosity (PP), carbonate (C) patchwork and hematite (Hm) cement in plane polarized light 100X

Goethite did not occur with any carbonates but rather with hematite as coatings. The variations in rock color within the Central Oklahoma Aquifer are due to the differences in hematite abundance, size and clustering/patchwork of hematite grains.

Secondary Porosity

Hematite affects the sandstone constituents within the Garber-Wellington Formation by its association with secondary porosity (Figure 12). It is associated with secondary porosity through its high pH value of approximately 7 to 8 for Mn-rich hematite due to high meteoric waters flowing through the pore space. The more basic the sediments, the higher the pH will become. This is important because any grain that is in contact with the hematite will display secondary porosity. Secondary porosity as is seen in thin section for clastic rocks can occur as (1) partial dissolution, (2) molds, (3) inhomogeneity of packing, (4) oversized pores and "floating" grains, (5) elongate pores, (6) corroded grains, (7) honeycombed grains and (8) fractured grains (Scholle, 1979). Within the Garber Sandstone, secondary porosity was seen as dissolution of detrital grains such as removal of feldspars, carbonate rock fragments, calcite and dolomite cements. The quartz grains display corrosion on their surfaces when adjacent to nearby porosity, dissolution of feldspars and microfractures in quartz grains.

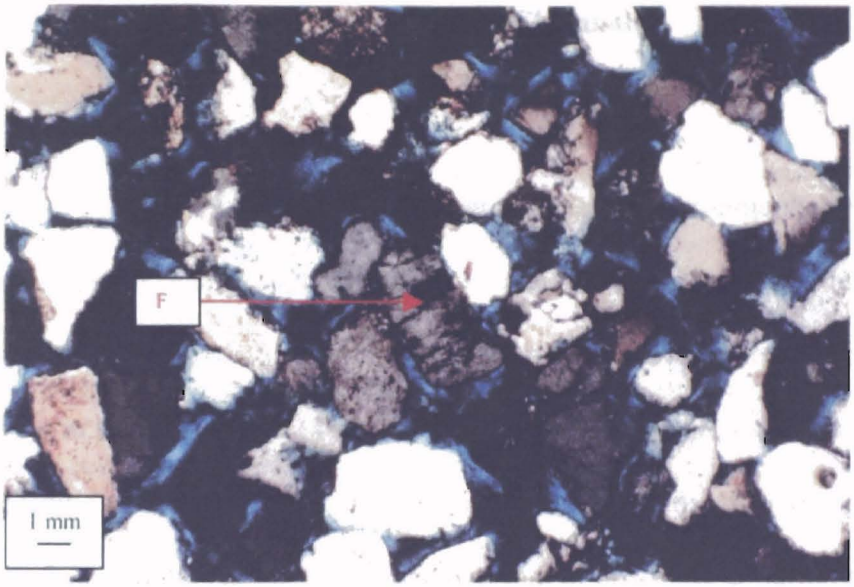


Figure 12 (a). Cross Nichols. Dissolution of feldspar grain (F) 100X

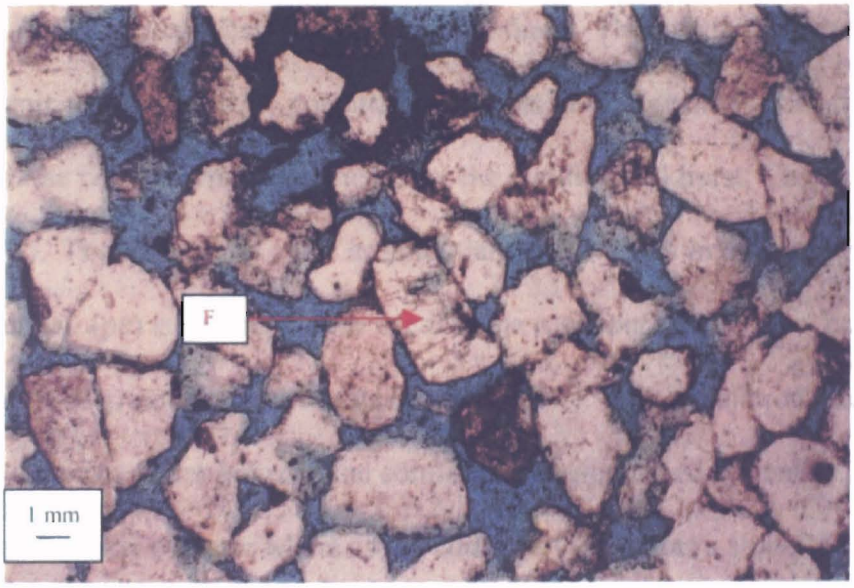


Figure 12 (b). Plane Polarized Light. Dissolution of feldspar grain (F) 100X

Water Chemistry

The water chemistry in natural groundwater environments have four important factors: (1) oxygen content of recharge water, (2) distribution and reactivity of organic matter and other potential reductants in the aquifer, (3) distribution of potential redox buffers in the aquifer and (4) circulation rate of the groundwater (Drever, 1997). According to the United States Geological Survey, the oxygen content of the recharge water found in the Garber Sandstone was that of post-oxic conditions. The dissolved oxygen was less than 1mg/L in the alluvium and terrace deposits and in the Garber Sandstone occurred mostly where the unit is confined by the Hennessey Group and in the deeper system where the unit is unconfined. The distribution and reactivity of organic matter and other potential reductants in the aquifer is almost completely absent from the core materials obtained from the aquifer (Parkhurst, Christenson and Breit, 1993). The iron oxides serve as potential redox buffers in the aquifer. Lower electron potential (pe) is generally slow because the reactions of the redox buffers per unit volume of groundwater are large (Drever, 1997). The circulation rate of the groundwater varies between the confined and unconfined systems. The shallow system has a fast flux of water where as the confined system has a slow flux of water.

According to the United States Geological Survey (Christenson and Havens, 1998), the water chemistry of the Central Oklahoma Aquifer is controlled by the uptake of carbon dioxide from the unsaturated zone of the Hennessey Group and dissolution of dolomite, biotite, chlorite, plagioclase and feldspar. The evidence to support the resulting water chemistry was petrographic and mass-balance geochemical modeling.

The dominant ions found in the groundwater of the confined parts of the Central Oklahoma Aquifer were calcium, magnesium and bicarbonate in the Garber-Wellington Formation. The dominant ions found in the Hennessey Group and the confined parts of the aquifer that includes that Garber-Wellington Formation are the Chase, Council Grove and Admire Group are sodium and bicarbonate. The sodium bicarbonate water is derived from the magnesium, calcium, and bicarbonate water by cat-ion exchange of calcium and magnesium with sodium in clay minerals (Christenson and Havens, 1998).

The Central Oklahoma Aquifer in the confined and unconfined areas has an oxic or post-oxic oxidation-reduction environment as indicated by the USGS calculations of the dissolved concentrations of oxygen, nitrate, arsenic (V), chromium (VI), selenium (VI), vanadium and uranium (Christenson and Havens, 1998).

The three flow regimes of the aquifer are shallow, deep and confined. The geochemical processes for the three flow regimes occurred each to a different extent. The shallow system has a rapid flux of water to remove dolomite, calcite and exchangeable sodium. The deep system in the unconfined part of the Garber-Wellington Formation has a flux of water that removes the exchangeable sodium. The carbonate minerals remain to maintain dolomite and calcite equilibrium. The confined system has the slowest groundwater flow and reactions are not sufficient enough to remove carbonate minerals or exchangeable sodium on clay (Christenson and Havens, 1998).

The water chemistry of the aquifer is very important because the Central Oklahoma Aquifer is the dominant aquifer in Oklahoma. It is the main source of water for the Oklahoma City area and surrounding vicinities. Ground water originates as

recharge from precipitation and discharges to streams and wells. Water flows rapidly through shallow, unconfined parts but can take years to flow through the confined part of the aquifer. The aquifer is unconfined in the eastern two thirds and confined in the western one third by the Hennessey Group (Figure 13). The overall quality of water in the aquifer is good but there are problems. The chemical problems are related to arsenic, chromium, selenium and uranium and urban problems of pesticides and organic compounds (Christenson and Havens, 1998).

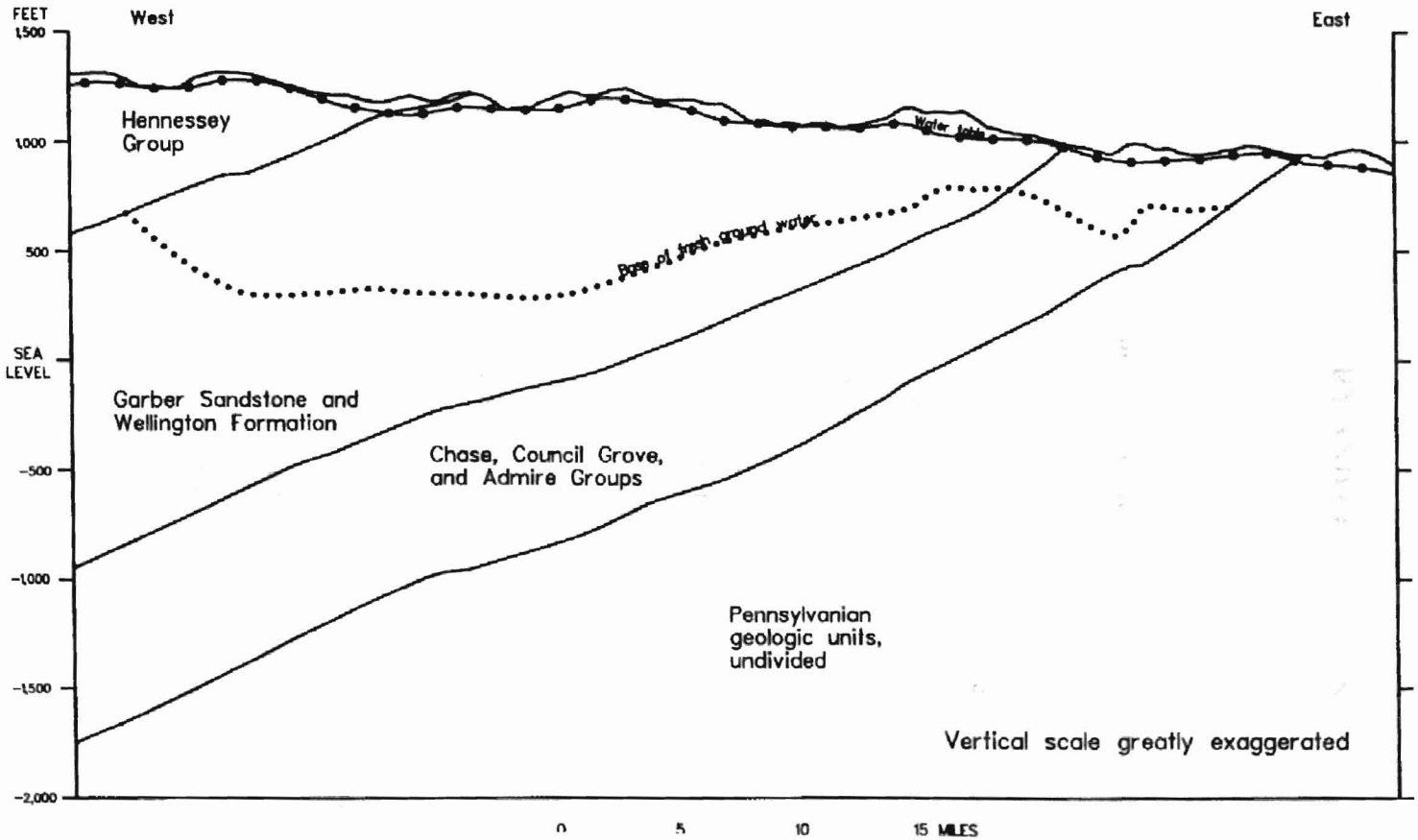


Figure 13. Geohydrologic section along latitude35^0 30' (Parkhurst, Christenson and Breit, 1993)

CHAPTER SEVEN

SUMMARY AND CONCLUSION

The objectives of this study which investigates the Garber Sandstone of the Garber-Wellington Formation located in the vicinity of City of Edmond, Oklahoma County, Oklahoma are (1) to document the relationships of the framework grains to the cements, (2) determine porosity type(s), (3) establish the diagenetic sequence for the Garber-Wellington Formation in the Central Oklahoma Aquifer, and (4) determine the geochemistry of iron oxide cements in the Garber Sandstone.

The results of this study are summarized as follows:

(1) The Garber Sandstone is a quartz arenite that contains monocrystalline quartz, feldspars and rock fragments. The authigenic constituents are dolomite, calcite, illite and hematite. The relationship of the grains and cements is the diagenesis that led to the formation of the authigenic constituents through chemical weathering in the form of pore-filling cements and coatings.

(2) The dominant cements are carbonates in the forms of dolomite and calcite and iron oxides in the forms of hematite and goethite as seen in thin section.

(3) The dominant porosity type is primary as intergranular porosity. The important porosity that was examined was secondary porosity in the forms of dissolution of grains, corroded grains, moldic and veins.

(4) The diagenetic sequence of events for the Garber-Wellington Formation includes the following: deposition, burial and exposure that began during the Permian. The detrital grains were dissolved and or altered and authigenic cements and

grains were dissolved and precipitated due to the change in fluid composition in the pore space during diagenesis.

(5) The geochemistry of iron oxides in the Garber Sandstone is a complex one that involves the formation of goethite and hematite through different pore waters and environmental interactions.

Recommendations for further analysis, involving Permian age rocks that include the Garber Sandstone and the overlying Hennessey Group are: (1) XRD analysis of clay minerals in the Central Oklahoma Aquifer to have a better understanding of the chemical make-up of the matrix and (2) geochemical and groundwater studies performed on the yellow goethite zones in the Garber Sandstone to have an understanding of the reduction zones.

SELECTED BIBLIOGRAPHY

Carpenter, R. H., Timothy, A. P., and Smith, R. L. (1975). Fe-Mn Oxide Coatings in Stream Sediments Geochemical Surveys: Journal of Geochemical Exploration, v. 4., 349-363 p.

Christenson, S. and Havens, J. (eds.). (1998). Ground-Water-Quality Assessment of the Central Oklahoma Aquifer, Oklahoma: Results of Investigations: United States Geological Survey, Water-Supply Paper 2357-A. Washington, DC: US Government Printing Office, 179 p.

Cornel, R. M., and Schwertmann, U. (1996). The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses: VCH, Germany, 570 p.

Cox, E. (1978). Subsurface Geochemical Exploration of Stratabound Copper in Lower Permian Redbeds in North-Central Oklahoma: Unpublished master dissertation, Oklahoma State University, Stillwater.

Dorn, R. (1998). Red Coatings: Elservier, New York, 429 p.

Drever, J. (1997). The Geochemistry of Natural Waters: Surface and Groundwater Environments (3rd edition) Prentice Hall: New Jersey

Folk, R. L. (1980). Petrology of Sedimentary Rocks: Hemphill Publishing Company, Austin, Texas, 185p.

Garrels, R. M. and Mackenzie, F. T. (1971). Evolution of Sedimentary Rocks: W.W. Norton and Company. Inc., New York, 397 p.

Krauskopf, K. and Bird, D. (1995). Introduction to Geochemistry: WCB McGraw-Hill, New York, 647p.

Miller, W. J. (1942). An Introduction to Historical Geology With Special Reference to North America: D. Can Nostrand Company, Inc., New York, 499 p.

Parkhurst, D. L., Christenson, S. and Breit, G. N. (1993). Ground-Water Quality Assessment of the Central Oklahoma Aquifer, Oklahoma Geochemical and Geohydrologic Investigations: United States Geological Survey. Open-File Report 92-642. Washington, DC: US Government Printing Office, 113 p.

Petersen, M. S., Rigby, J. K. and Hintze, L. F. (1973). Historical Geology of North America: Wm. C. Brown Company Publishers, Dubuque, Iowa. 231 p.

Scheidegger, A., Borkovec, M. and Sticher, H. (1993). Coating of Silica Sand With Goethite: Preparation and Analytical Identification. Geoderma, 58: 43-65.

Schmalz, R. F. (1968). Formation of Red Beds in Modern and Ancient Deserts: Geol. Soc. Am. Bull., Vol. 79, p. 277-280.

Scholle, P. (1979). A Color Illustrated Guide to Constituents, Textures, Cements, and Porosities of Sandstone and Associated Rocks. AAPG Memoir 28, Tulsa, Oklahoma.

Scholle, P. A. Peryt, T. M. and Ulmer-Scholle, D. S. (Eds.). (1995). The Permian of Northern Pangea Volume 1: Paleogeography, Paleoclimates, Stratigraphy: Springer-Verlag, New York, 261 p.

Turner, P. (1980). Developments in Sedimentology, Continental Red Beds. ElSevier Scientific Publishing Co., Vol. 29.

Walker, T. R. (1967a). Formation of Red Beds in Modern and Ancient Deserts. Geol. Soc. Am. Bull., 78: 353-368.

Walker, T.R (1967b). Color of Recent Sediments in tropical Mexicos: A Contribution to the Origin of Red Beds. Geol. Soc. Am. Bull., 78: 917-920.

Yariv, S. and Cross, H. (1979). Geochemistry of Colloid Systems For Earth Scientists: Springer-Verlag, New York, 450 p.

APPENDIX A

Appendix A-Outcrop Constituents of the Garber Sandstone From Petrographic Analysis

CONSTITUENTS		AR-A-V	AR-B-V	ED-Aa-V	ED-Ab-V	ED-Ac-V
DETRITAL						
Quartz						
	Monocrystalline	53	56.6	61.8	60.9	56.7
	Polycrystalline				2.9	
Feldspar						
	Orthoclase					
	Plagioclase					1
Rock Fragments						
	Shale					
	Chert				0.6	
	Siltstone					
	Carbonate					
	Metamorphic					
Other Grains						
	Shell Fragments					
	Muscovite					1.4
	Biotite					
	Zircon					
	Tourmaline					
	Collophane					
Illite						1.8
AUTHIGENIC						
Cements						
	Quartz					
	Syntaxial					
	Chalcedony					
	Carbonate			3.6		
	Calcite				8.8	9.4
	Dolomite					
	Siderite					
	Chamosite Pellet					
	Glauconite					
	Clays					
	Kaolinite					
	Chlorite					
	Illite					
	Hematite	20.5	23.1		12.7	14.3
	Limonite			6.1		
	Pyrite					
POROSITY						
	Thin Section Porosity	26.5	20.3	28.5	14.1	15.4
TOTAL DETRITAL						
	Quartz	53	56.6	61.8	63.8	56.7
	Feldspar					1
	Rock Fragments				.6	
TOTAL		100	100	100	100	100
TOTAL CLAYS						1.8
TOTAL CARBONATES						
	Detrital					
	Cement			3.6	8.8	9.4
TOTAL QUARTZ						
	Quartz grains	53	56.6	61.8	63.8	56.7
	Quartz cements					
TOTAL CONSTITUENTS		100	100	100	100	100
TOTAL ROCK		100	100	100	100	100

Appendix A-Outcrop Constituents of the Garber Sandstone From Petrographic Analysis

CONSTITUENTS		ED-B-V	ED-C-V	ED-D-H	ED-E-V	ED-F-V
DETRITAL						
Quartz						
	Monocrystalline	21.2	40.2	51.3	71.4	59.5
	Polycrystalline		3.4.2.6			
Feldspar						
	Orthoclase					
	Plagioclase		1.8	1.2	3.2	
Rock Fragments						
	Shale					
	Chert			2.8		
	Siltstone					
	Carbonate	32.4	6			
	Metamorphic					
Other Grains						
	Shell Fragments					
	Muscovite					
	Biotite					
	Zircon			.9		
	Tourmaline					
	Collophane					
Illite		10	5.9			
AUTHIGENIC						
Cements						
	Quartz					
	Syntaxial					
	Chalcedony					
	Carbonate					
	Calcite		1.4	7.9	4.9	14.3
	Dolomite		30			
	Siderite					
	Chamosite Pellet					
	Glauconite			1.5		
	Clays					
	Kaolinite					
	Chlorite					
	Illite					
	Hematite	32.8	4.6	4.7	5.4	18
	Limonite					
	Pyrite					
POROSITY						
	Thin Section Porosity	3.6	6.7	27.1	15.1	8.2
TOTAL DETRITAL						
	Quartz	21.2	43.6	53.9	71.4	59.5
	Feldspar		1.8	1.2	3.2	
	Rock Fragments	32.4	6	2.8		
TOTAL		100	100	100	100	100
TOTAL CLAYS		10	5.9			
TOTAL CARBONATES						
	Detrital	32.4	6			
	Cement		31.4	7.9	4.9	14.3
TOTAL QUARTZ						
	Quartz grains	21.2	43.6	53.9	71.4	59.5
	Quartz cements					
TOTAL CONSTITUENTS		100	100	100	100	100
TOTAL ROCK		100	100	100	100	100

Appendix A-Outcrop Constituents of the Garber Sandstone From Petrographic Analysis

CONSTITUENTS		ED-G-V	ED-Ha-V	ED-Hb-V	ED-I-H	ED-Ia-V
DETRITAL						
Quartz						
	Monocrystalline	53.9	62	46	9.2	25.8
	Polycrystalline	2.1	1.7	1.6		
Feldspar						
	Orthoclase					
	Plagioclase	2.2	1.2	3.3		1
Rock Fragments						
	Shale					
	Chert	3.5		2.5		
	Siltstone					
	Carbonate					12.6
	Metamorphic					
Other Grains						
	Shell Fragments					
	Muscovite					
	Biotite					
	Zircon	5.3	.7	.3		
	Tourmaline					
	Collophane					
Illite						7.9
AUTHIGENIC						
Cements						
	Quartz					
	Syntaxial					
	Chalcedony					
	Carbonate					
	Calcite		11.9			11.1
	Dolomite				36.6	28.4
	Siderite					
	Chamosite Pellet					
	Glauconite					
	Clays					
	Kaolinite					
	Chlorite					
	Illite					
	Hematite	7.7	5.8	28.8	53	11.9
	Limonite					
	Pyrite	3				
POROSITY						
	Thin Section Porosity	22.3	16.7	17.5	1.2	1.3
TOTAL DETRITAL						
	Quartz	56	63.7	47.6	9.2	25.8
	Feldspar	2.2	1.2	3.3		1
	Rock Fragments	3.5		2.5		12.6
TOTAL		100	100	100	100	100
TOTAL CLAYS						7.9
TOTAL CARBONATES						
	Detrital					12.6
	Cement		11.9		36.6	39.5
TOTAL QUARTZ						
	Quartz grains	56	63.7	47.6	9.2	25.8
	Quartz cements					
TOTAL CONSTITUENTS		100	100	100	100	100
TOTAL ROCK		100	100	100	100	100

Appendix A-Outcrop Constituents of the Garber Sandstone From Petrographic Analysis

CONSTITUENTS		ED-Ib-V	ED-J-V	ED-L-V	ED-M-V	ED-N-V
DETRITAL						
Quartz						
	Monocrystalline	17.7	23.8	14.8	56.7	65.4
	Polycrystalline				4.9	
Feldspar						
	Orthoclase					
	Plagioclase	1.2			.8	
Rock Fragments						
	Shale					
	Chert				2.3	
	Siltstone			2.9	10	
	Carbonate		7.7	44.4		
	Metamorphic					
Other Grains						
	Shell Fragments					
	Muscovite					
	Biotite					
	Zircon		.6		2.2	
	Tourmaline					
	Collophane					
Illite				10		
AUTHIGENIC						
Cements						
	Quartz					
	Syntaxial					
	Chalcedony					
	Carbonate					
	Calcite	24.3				
	Dolomite	24.2	41.1	8.9		
	Siderite					
	Chamosite Pellet					
	Glauconite					
	Clays					
	Kaolinite					
	Chlorite					
	Illite					
	Hematite	30.1	26.8	10.1	1.1	8.6
	Limonite					
	Pyrite					.8
POROSITY						
	Thin Section Porosity	2.5		8.9	22	25.2
TOTAL DETRITAL						
	Quartz	17.7	23.8	14.8	61.6	65.4
	Feldspar	1.2			.8	
	Rock Fragments		7.7	47.3	12.3	
TOTAL		100	100	100	100	100
TOTAL CLAYS						
TOTAL CARBONATES						
	Detrital		7.7	44.4		
	Cement	48.5	41.1	8.9		
TOTAL QUARTZ						
	Quartz grains	17.7	23.8	14.8	61.6	65.4
	Quartz cements					
TOTAL CONSTITUENTS		100	100	100	100	100
TOTAL ROCK		100	100	100	100	100

Appendix A-Outcrop Constituents of the Garber Sandstone From Petrographic Analysis

CONSTITUENTS		ED-N-H	ED-O-V	ED-P-V	ED-Q-V	ED-R-V
DETRITAL						
Quartz						
	Monocrystalline	48.3	38.8	34.7	65.3	66.2
	Polycrystalline					
Feldspar						
	Orthoclase					
	Plagioclase				3	
Rock Fragments						
	Shale					
	Chert					
	Siltstone					
	Carbonate					
	Metamorphic					
Other Grains						
	Shell Fragments					
	Muscovite					
	Biotite					
	Zircon		.9			
	Tourmaline				1.7	
	Collophane					
Illite			5.8			
AUTHIGENIC						
Cements						
	Quartz					
	Syntaxial					
	Chalcedony					
	Carbonate					
	Calcite		19	2.9		.5
	Dolomite		28.3	5		
	Siderite					
	Chamosite Pellet					
	Glauconite					
	Clays					
	Kaolinite					
	Chlorite					
	Illite					
	Hematite	35.7	5.5	28.2	.7	5.5
	Limonite					
	Pyrite					
POROSITY						
	Thin Section Porosity	16	1.7	3.1	29.5	27.8
TOTAL DETRITAL						
	Quartz	48.3	38.8	34.7	65.3	66.2
	Feldspar				3	
	Rock Fragments					
TOTAL		100	100	100	100	100
TOTAL CLAYS			5.8			
TOTAL CARBONATES						
	Detrital					
	Cement		47.3	7.9		.5
TOTAL QUARTZ						
	Quartz grains	48.3	38.8	34.7	65.3	66.2
	Quartz cements					
TOTAL CONSTITUENTS		100	100	100	100	100
TOTAL ROCK		100	100	100	100	100

Appendix A-Outcrop Constituents of the Garber Sandstone From Petrographic Analysis

CONSTITUENTS		ED-S-V	ED-T-V	ED-U-V	ED-U-H
DETRITAL					
Quartz					
	Monocrystalline	42.4	61.8	64.5	67.4
	Polycrystalline				
Feldspar					
	Orthoclase				
	Plagioclase			3.5	2.5
Rock Fragments					
	Shale				
	Chert				
	Siltstone				
	Carbonate				
	Metamorphic				
Other Grains					
	Shell Fragments				
	Muscovite			2.5	
	Biotite				
	Zircon	.8			
	Tourmaline				
	Collophane				
Illite					
AUTHIGENIC					
Cements					
	Quartz				
	Syntaxial				
	Chalcedony				
	Carbonate				
	Calcite				
	Dolomite				
	Siderite				
	Chamosite Pellet				
	Glauconite				
	Clays				
	Kaolinite				
	Chlorite				
	Illite				
	Hematite	19.7	8.1	8	8.7
	Limonite				
	Pyrite				
POROSITY					
	Thin Section Porosity	37.1	30.1	21.5	21.4
TOTAL DETRITAL					
	Quartz	42.4	61.8	64.5	67.4
	Feldspar			3.5	2.5
	Rock Fragments				
TOTAL		100	100	100	100
TOTAL CLAYS					
TOTAL CARBONATES					
	Detrital				
	Cement				
TOTAL QUARTZ					
	Quartz grains	42.4	61.8	64.5	67.4
	Quartz cements				
TOTAL CONSTITUENTS		100	100	100	100
TOTAL ROCK		100	100	100	100

VITA

Jessica Eileen Witt

Candidate for the Degree of

Master of Science

Thesis: THE DIAGENESIS AND PETROLOGY OF IRON OXIDES IN THE GARBER-WELLINGTON FORMATION

Major Field: Geology

Biographical:

Personal Data: Born in Brick, New Jersey, On April 28, 1977, the daughter of Asa and Rosalyn Witt.

Education: Graduated from Brick Memorial High School, Brick New Jersey in June 1995; received Bachelor of Science degrees in Geology and Geography from Northwest Missouri State University, Maryville, Missouri in May 1999. Completed the requirements for the Master of Science degree with a major in Geology at Oklahoma State University in May 2001.

Experience: Employed by Oklahoma State University, Department of Geology as a Graduate Teaching and Research Assistant, 1999 to May 2001.

Professional Membership: American Association of Petroleum Geologists.